



Original Research Paper

Pyrolysis of *Parinari polyandra* Benth fruit shell for bio-oil production

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HIGHLIGHTS

- Bio-oil production from non-conventional *Parinari polyandra* B. fruit shell is an intermediate pyrolysis process.
- Bio-oils were obtained using a fixed bed reactor within a temperature range of 375 - 550°C.
- The presence of valuable compounds suggests high potentials for industrial applications.
- The presence of acetic acids in bio-oil suggests the need to upgrade the oil before utilization as a fuel.

GRAPHICAL ABSTRACT



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ABSTRACT

Non-conventional agricultural residues such as *Parinari polyandra* Benth fruit shell (PPBFS) are potential sources of biomass feedstock that have not been investigated for bio oil production. In this study, PPBFS was pyrolyzed *via* an intermediate pyrolysis process for the production of bio oil. The bio oils were obtained using a fixed bed reactor within a temperature range of 375–550 °C and were characterized to determine their physicochemical properties. The most abundant organic compounds present were acetic acid, toluene, 2-cyclopenten-1-one, 2-furanmethanol, phenol, guaiacol and 2,6-dimethoxyphenol. The bio-oil produced at 550 °C possessed a higher quantity of desirable compounds than those produced at lower temperatures. The presence of acetic acids in the bio-oil suggested the need to upgrade the bio-oil before utilization as a fuel source.

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1. Introduction

There is a mounting interest in harnessing a variety of renewable resources for energy supply (IEA, 2011; Akia et al., 2014). This is the consequence of an increasing awareness on the need to find alternative forms of energy to address the negative effects of the use of fossil fuels on the environment. The growing energy needs of the world, the hike in global fuel prices as well as the depletion of the non-renewable fossil fuel reserves are also among the main reasons directing more research towards renewable fuels (E4tech, 2008; Akia et al., 2014; Kumar, 2014).

Biomass which is regarded as the third world largest primary energy resource has been a research focus for production of various types of alternative fuels including bio-oil (Bradely, 2006). This research focus has in turn necessitated the investigation of more biomass sources as feedstock. On the other hand, recently there has been an increase in research interest on biomass conversion via pyrolysis (IEA, 2011). Pyrolysis is one of the thermochemical conversion processes involving thermal decomposition of biomass usually above 400 °C in the absence of oxygen (Czemik and Bridgwater, 2004).

A vast number of plant materials including energy crops and various agricultural wastes are being considered as bio-oil feedstock (Abnisia et al., 2011; Omar et al., 2011; Garcia et al., 2012; Greenhalf et al., 2012; Park et al., 2012; Balan et al., 2014; Beetul et al., 2014.; Kumar, 2014). The quality of bio-oil obtained depends on the properties of the biomass as well as operating conditions (Park et al., 2012). Despite the fact that there have been various research works conducted on a number of energy crops and agricultural wastes for bio-oil production such as rice husk (Garcia et al., 2012), cassava rhizomes (Pattiya et al., 2008), miscanthus (Hodgson et al., 2010) corn stover and bagasse among others, there is still a growing need to investigate non-conventional biomass feedstock particularly those of no other applications such as *Parinari polyandra* Benth.

Parinari polyandra Benth is a savannah plant found in West Africa extending from Mali to Sudan. It is also known as *Maranthes polyandra* Benth, belonging to the family *Rosaceae*. The tree is about 8 m high with glossy leaves that are elliptical and are usually rounded at both ends. The fruits are smooth and about 2.5 cm long having a deep red or blackish purple color depending on the variety (Fig. 1). The endosperm has a yellow white appearance with a thick seed coat containing the oily mass. The fresh seed kernel contains between 31-60% oil depending on the variety and season of harvest (Olatunji et al., 1996).

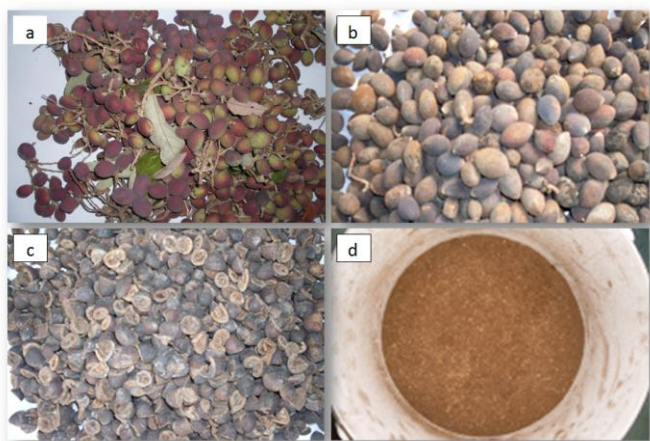


Fig.1. *Parinari polyandra* Benth fruits: (a) fresh (b) dried (c) without seed, and (d) milled.

Parinari polyandra Benth is currently very much under-utilized partly due to its non-edibility and also owing to lack of extensive research on the fruit and seeds. The main utilization has been that of the plants parts for traditional medicinal purposes (Iweala & Oludare, 2011). Although, the seed oil is considered not edible, it has been found to be suitable for preparation of alkyd resins of desirable properties (Odetoeye et al., 2013a, Odetoeye et al., 2014). The fruit shell, being a major waste generated from the seed oil utilization,

has been previously characterized (Odetoeye et al., 2013b; Titiloye et al., 2013). As reported in our previous work, the thermochemical properties obtained for *Parinari* fruit shell determined using ASTM standard methods including ultimate, inorganic, and proximate analyses as well as the higher heating value of 20.5 MJ/kg were positive indicators for bio-oil production as shown in Table 1. (Odetoeye et al., 2013b).

Table 1.

Proximate analysis, ultimate analysis, inorganic analysis and higher heating values of *Parinari polyandra* Benth fruit shell (Odetoeye et al., 2013 b).

Ultimate analysis	% (dry basis)	Inorganic analysis	ppm (dry basis)
C	48.04	Al	37
H	5.76	B	13
N	2.13	Ba	24
S	0.10	Ca	3600
Cl	0.44	Cd	ND*
O ^a	43.53	Cr	2
		Cu	8
		Fe	92
		Hg	1
		K	11200
Proximate analysis	%	Mg	1700
Moisture content	2.7	Mn	17
Ash content	4.7	Na	54
Volatile content	78.2	Ni	3
Fixed carbon	17.1	P	1200
		Pb	ND
		Rb	18
		Si	164
		Sr	14
Higher heating value	MJ/kg	Ti	4
Bomb calorimeter	20.50	V	1
Calculated HHV ¹	18.96	Zn	10
Calculated HHV ²	18.90		

*ND: not detected

^a Oxygen by difference

¹ (Channiwala & Parikh, 2002)

² (Wai, 2005)

In this study, we report for the first time the pyrolysis of *Parinari polyandra* Benth fruit shells in a fixed bed reactor and investigate its suitability as a new feedstock for bio-oil production via intermediate pyrolysis. To the best of our knowledge no pyrolysis work has been reported on *Parinari polyandra* Benth before.

2. Materials and methods

2.1. Materials

Parinari polyandra Benth fruits were collected from trees at the University of Ilorin, Ilorin, Nigeria (8°30'N 4° 33'E) during the month of November. The fruits were cut into halves to remove the seeds from the woody endocarp and were subsequently sun-dried for five days. The dried fruits were ground using a Retsh SM 200 heavy-duty cutting mill fitted with a 2 mm particle size screen. The samples were characterized and compared to other similar biomasses.

2.2. Methods

2.2.1. Pyrolysis procedure

The intermediate pyrolysis experiments were carried out on a bench scale fixed-bed reactor at reaction temperatures of 550, 450 and 375 °C. The reactor was made of quartz glass tube with an internal diameter of 30 mm and a height of 390 mm. It was connected to a primary condenser used for the collection of condensable bio-oil. The non-condensable gases released were scrubbed with isopropanol before sending a stream of the gases to the GC-TCD HP Series II and the remaining gases vented through the fume cupboard.

The experimental set up is as shown in Figure 2. Nitrogen gas flow into the reactor was maintained at a flow rate of 50 cm³/min. The heating rate of the reactor was 25°C/min. The bio-oils were obtained from the oil pots,

condenser and the connecting tube after each experimental run. The bio-oil produced was initially in a gaseous phase when leaving the reactor at a relatively fast rate due to the high temperatures used. On reaching the bottle-like condensers filled with dry ice, the condensable gases turned into liquid in the condenser. The secondary condenser implemented in the system ensured that the adequate condensation was achieved. The bio-oil samples used for the subsequent analyses were collected mainly from the oil pot and the condensers without the use of a solvent.

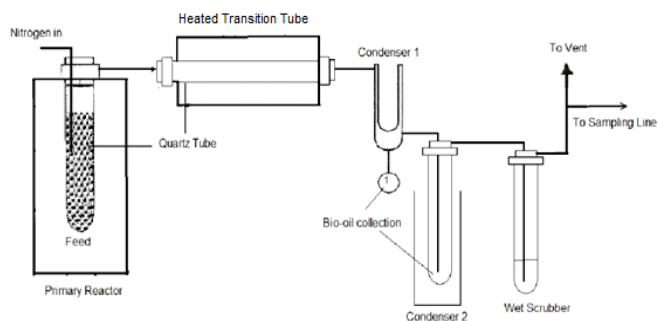


Fig.2. Experimental set up for intermediate pyrolysis experiment

The bio-oil yield was calculated considering the oil entrapped in the glassware condensers, by weighing each part of the glassware apparatus before and after each pyrolysis experiment. The biochar yield was also measured by weighing the reactor tube and the reactor head before and after the reaction since the char (solid) remained mainly in the reactor tube and head after the reaction. The mass of the non-condensable gases was obtained by difference. The effects of reaction temperatures (375, 450 and 550 °C) on products yield and properties were also investigated

2.3. Bio-oil characterization

The bio-oil products obtained were characterized to determine their quality and composition.

2.3.1. Density, pH and water content determinations

The pH values of the bio-oils prepared were determined using a Sartorius pH meter model PB-11. Mettler Toledo Portable Lab Densimeter was used to determine the density of the bio-oil samples. Water content was determined using the Karl Fischer volumetric titration method based on the ASTM D1744 standard

2.3.2. Heating value and elemental analysis

The elemental analysis of the parinari shell bio-oil was carried out by MEDAC Ltd. Surrey, U.K. A unified correlation approach was employed to calculate the higher heating values (HHV) using an empirical equation suggested by Saidure et al.(2011):

$$\text{HHV} = 0.3516 (\text{C}) + 1.16225 (\text{H}) - 0.1109 (\text{O}) + 0.0628 (\text{N}) + 0.10465 (\text{S}) \quad (\text{Eq. 1})$$

2.3.3. Gas chromatograph-mass spectrometer (GC-MS) analysis

The composition of the bio-oil produced was determined using the Hewlett Packard 5890 Series II Gas Chromatograph equipped with a Hewlett Packard 5972 mass selective detector. Helium was used as the carrier gas with a DB 1706 non-polar capillary column. The initial oven temperature was 40 °C and ramped up to 290 °C at a rate of 3 °C/min. The injection temperature was held at 310 °C with a volume of 5µl. The dilution solvent used was ethanol and the dilution rate was 1:5. Identification of compounds in the spectral and chromatograph data was done with the aid of NIST mass spectra database.

3. Results and discussion

3.1. Effect of temperature on yield

As shown in Figure 3, relatively higher liquid yield was obtained when the pyrolysis experiment was run at 550 °C compared to 375 and 450 °C suggesting that the liquid product yield increased by increasing the temperature. The 550 °C run was also characterized with relatively lower char content of 35.6%, while the highest char content of the product was obtained at 375 °C.

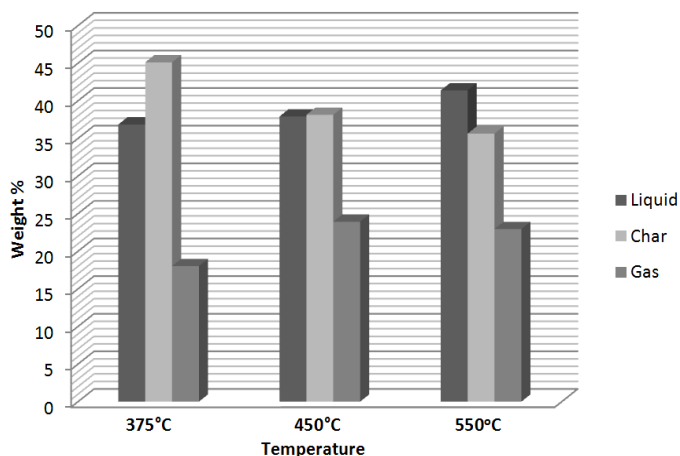


Fig.3. Product yield distribution of Parinari fruit shell obtained through pyrolysis at different temperatures

The liquid and char products obtained at 450 °C were of comparable values. The liquid product yield tended to increase with the rise in process temperature. This trend observed in the product yield distribution is similar to the pyrolysis results obtained by Volli and Singh for sesame, mustard and neem de-oiled cakes (Volli&Singh, 2012). The relatively higher temperature required for the parinari biomass to decompose into favorable liquid product may be due to the high lignin concentration of 30 wt. % yielding phenols and phenolic compounds (Kim et al., 2012; Titiloye et al., 2013).

The biochar yield at 450 and 550 °C are relatively close in percentage value. This observation is actually in line with the thermogravimetric analysis result reported in our earlier work (Odetoye et al., 2013b). In fact, the decomposition of cellulose and hemicellulose which are the main components occurred before 450 °C while lignin decomposition occurred relatively slower at around 400 °C, hence, little difference was observed in the biochar yield after 400 °C.



Fig.4. Parinari polyandra fruit shell bio-oil samples

3.2. Bio-oil characterization

The bio-oil samples obtained were dark brown in colour (Fig.4) and were composed of aqueous and organic phases which were relatively semi-homogenous. The liquids were observed to separate completely into 2 phases when stored. The parinari bio-oil exhibited homogenous characteristics and free flowing properties. The pH of the bio-oil tended to increase with increasing processing temperature and the sample prepared at 550 °C had the highest pH of 4.56 (Table 2).

Table 2.
Some of the physical and chemical properties of the bio-oil prepared (organic phase)

Properties	Unit	375 °C	450 °C	550 °C
pH		4.12	4.32	4.56
Density	g/cm ³	1.043	1.027	1.021
Water content	wt %	13.995	16.17	14.78
Elemental composition	wt %			
C		44.74	66.43	69.31
H		9.15	8.28	8.97
N		1.27	2.73	2.89
O*		44.27	21.38	18.79
S		0.52	0.79	0.73
Cl		<0.05	0.42	<0.05
HHV	MJ/kg	21.85	30.76	32.84
Empirical Formula		CH _{2.45} O _{0.74} N _{0.02}	CH _{1.5} O _{0.24} N _{0.04}	CH _{1.55} O _{0.20} N _{0.04}
H/C molar ratio		2.5	1.5	1.6
O/C molar ratio		0.74	0.24	0.2

The calculated heating value of 30.76 MJ/kg for the bio-oil obtained through pyrolysis at 450 °C was comparable to those of some other biomasses reported in the literature. More specifically, it is slightly higher than 26.22 MJ/kg obtained for corncob (Demiralet al., 2012) and comparable to the 30 MJ/kg of neem seed cake bio-oil (Vollli & Singh, 2012). The elemental analysis of the parinari bio-oil showed that the oxygen content decreased as the pyrolysis temperature increased, suggesting the deoxygenation reaction taking place. The chlorine content was relatively higher while the sulphur content was desirably low in parinari bio-oil. Hence, there is a lower risk of sulphur dioxide formation.

3.3. Bio-oil chemical composition

The bio-oils consisted of a complex mixture of various compounds. The GC-MS chromatogram for a typical parinari fruit shell sample pyrolysis oil is shown in Figure 5. The most prominent peaks identified, corresponding chemical names, retention times, chemical formula, molecular weights and peak areas measured are summarised in Table 3 and Figures 6, 7, 8 and 9. The identified compounds included alkenes, phenols, carboxylic acids and their derivatives reported for the bio-oils obtained from some other biomasses (Vollli & Singh, 2012). As presented in Figure5, the main constituents in parinari bio-oil were acetic acid, toluene, 2-cyclopenten-1-one, 2-furanmethanol, phenol, guaiacol and 2,6-dimethoxyphenols. Phenolic compounds such as guaiacol and 2,6-dimethoxyphenol are among the valuable components that can be obtained from bio-oil (Demiral et al, 2012)

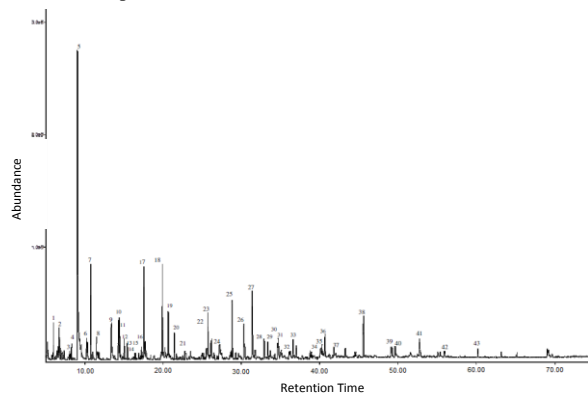


Fig.5. A typical GC-MS chromatogram for *Parinari polyandra* bio-oil

Table 3.
Most prominent identified compounds of Parinari bio-oil

Peak ID	RT (min)	Compound Name	Formulae	RMM*	Area % 375°C	Area % 450°C	Area % 550°C
1	6.048	2-methylfuran	C ₅ H ₆ O	82.10	0.51	0.96	1.25
2	6.772	2-butanone	C ₄ H ₈ O	72.11	0.71	1.45	1.38
3	8.083	2-methylbutanal	C ₅ H ₁₀ O	86.13	0.25	0.38	0.29
4	8.336	2,5-Dimethylfuran	C ₆ H ₈ O	96.13	0.15	0.53	0.49
5	9.083	Acetic Acid	C ₂ H ₄ O ₂	60.05	18.96	18.2	13.4
6	10.267	Hydroxyacetone	C ₃ H ₆ O ₂	74.08	1.18	0.8	0.66
7	10.784	Toluene	C ₇ H ₈	92.14	0.65	3.67	5.28
8	11.509	Pyridine	C ₅ H ₅ N	79.10	0.73	1.29	0.77
9	13.429	Propanoic acid	C ₃ H ₆ O ₂	74.08	1.6	2	1.21
10	14.372	Cyclopentanone	C ₅ H ₈ O	84.12	0.62	1.7	1.43
11	14.51	1-hydroxy-2-butanone	C ₄ H ₈ O ₂	88.11	1.1	0.76	-
12	15.05	Ethylbenzene	C ₈ H ₁₀	106.17	-	0.82	1.32
13	15.441	p-Xylene	C ₈ H ₁₀	106.17	-	0.7	1.54
14	16.464	Cyclohexanone	C ₆ H ₁₀ O	98.14	-	0.28	0.33
15	16.901	m-Xylene	C ₈ H ₁₀	106.17	0.21	0.28	0.6
16	17.269	Styrene	C ₈ H ₈	104.15	-	0.57	0.75
17	17.603	2-Cyclopenten-1-one	C ₅ H ₆ O	82.10	4.03	4.51	3.84
18	19.936	2-Furanmethanol	C ₅ H ₈ O ₂	98.10	5.98	4.66	3.76
19	20.661	2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	96.13	1.31	2.09	2.23
20	21.431	2-Furyl Methyl Ketone	C ₆ H ₆ O ₂	110.11	1.27	1.33	1.22
21	23.535	2-hydroxy-2-cyclopenten-1-one	C ₅ H ₆ O ₂	98.00	1.09	0.72	-
22	25.731	3-Methyl-2-Cyclopentenone	C ₆ H ₈ O	96.13	1.84	2.67	2.55
23	26.226	Tetrahydro-2-furanmethanol	C ₅ H ₁₀ O ₂	102.13	2	1.12	1.13
24	27.249	2,4-dimethyl-2-oxazoline-4-methanol	C ₆ H ₁₁ NO ₂	129.16	0.23	1.38	0.82
25	28.813	Maple lactone / 2-hydroxy-3-methyl-2-cyclopenten-1-one	C ₆ H ₈ O ₂	112.13	4.28	3.62	3.48
26	30.353	Phenol	C ₆ H ₆ O	94.11	1.11	2.06	4.19
27	31.377	Guaiacol	C ₇ H ₈ O ₂	124.14	5.39	3.86	3.49
28	32.883	2-Methylphenol	C ₇ H ₈ O	108.14	0.36	1.04	2.36
29	33.4	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	C ₇ H ₁₀ O ₂	126.15	1.45	0.91	0.81
30	34.619	p-cresol	C ₇ H ₈ O	108.14	0.55	0.83	1.51
31	34.711	m-Cresol	C ₇ H ₈ O	108.14	0.37	1.33	3.58
32	36.585	Isocresol / 5-methylguaiacol	C ₈ H ₁₀ O ₂	138.17	1.38	0.91	0.8
33	37.01	2,4-Dimethylphenol	C ₈ H ₁₀ O	122.16	0.29	0.65	1.6
34	39.045	4-Ethylphenol	C ₈ H ₁₀ O	122.16	-	0.2	0.5
35	40.161	Dianhydromannitol	C ₆ H ₁₀ O ₄	146.14	1.06	0.95	0.76
36	40.666	4-Ethylguaiacol	C ₈ H ₁₀ O ₂	152.19	1.64	1.29	1.33
37	41.862	1,4:3,6-dianhydro-α-d-glucopyranose	C ₆ H ₈ O ₄	144.13	1.02	0.68	0.65
38	45.576	2,6-Dimethoxyphenol	C ₈ H ₁₀ O ₃	154.17	5.51	2.44	2.23
39	49.175	Isoeugenol	C ₁₀ H ₁₂ O ₂	164.20	1.36	0.55	0.9
40	49.623	4-methoxy-3-(methoxymethyl)-phenol	C ₉ H ₁₂ O ₃	168.19	2.29	0.98	1.24
41	52.762	1,2,3-trimethoxy-5-methylbenzene	C ₁₀ H ₁₄ O ₃	182.22	2.05	1.12	1.23
42	55.924	2,4-hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (EZ)-	C ₁₂ H ₁₈ O ₄	226.00	-	0.47	0.52
43	60.155	4-Allyl-2,6-dimethoxyphenol	C ₁₁ H ₁₄ O ₃	194.23	1.34	0.57	0.92
TOTAL					75.87	77.33	78.35

*Relative molecular mass

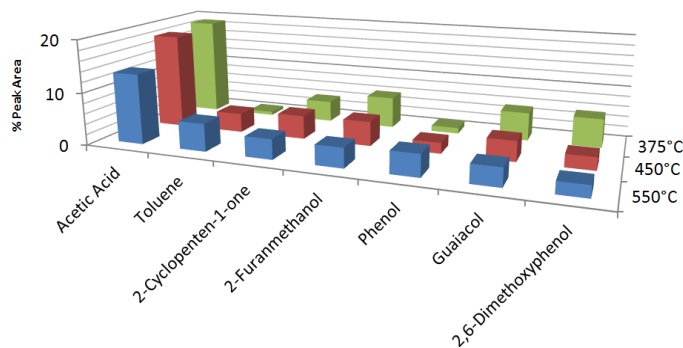


Fig.6. Main chemical constituents of Parinari fruit shell bio-oil.

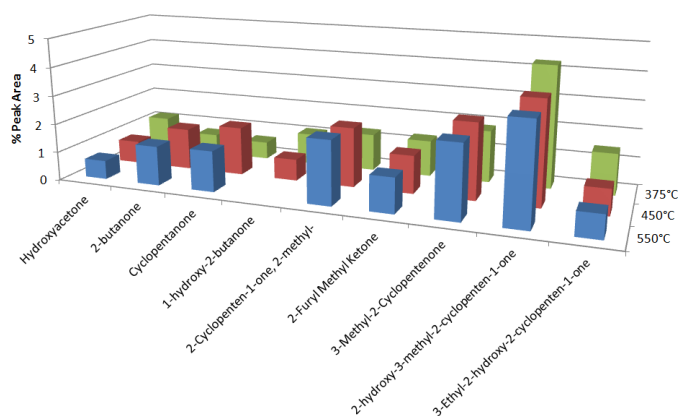


Fig.7. Main ketone constituents in Parinari fruit shell bio-oil.

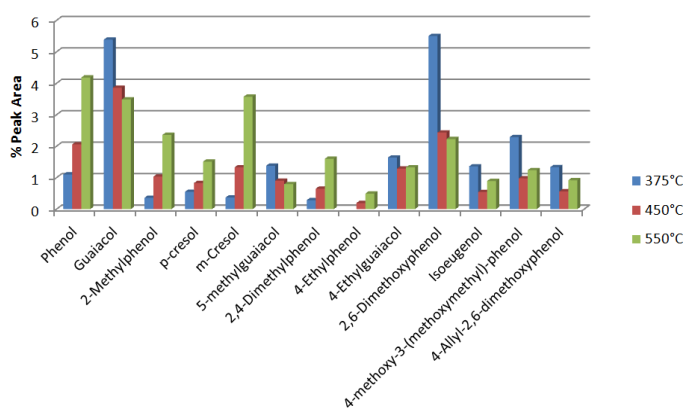


Fig.8. Phenol and its derivatives in Parinari fruit shell bio-oil.

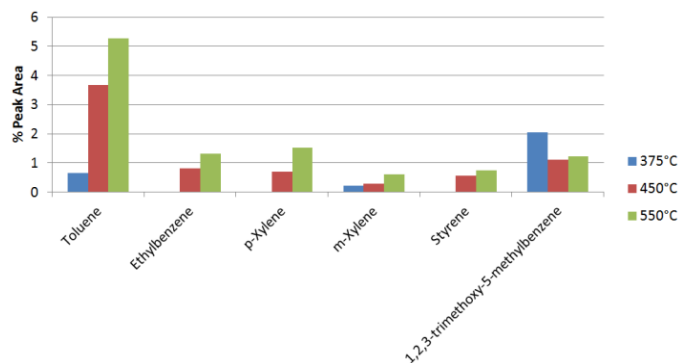


Fig.9. Main BTX aromatic hydrocarbons in Parinari fruit shell bio-oil.

The highest temperature of 550 °C favored the production of phenolic compounds and their derivatives while the oxygenated phenolic derivatives were produced at lowest temperature of 375 °C. The significant presence of phenolics and aromatics in the bio-oil can be attributed to lignin which is a phenolic bio-polymer (Park et al., 2012). Acetic acid is the main organic acid contributing up to 19% peak area. The presence of these organic acids is associated with low pH values measured for the bio-oil and are generally known to be undesirable in bio-oils. The increase in pH achieved by increasing the pyrolysis temperature correlated with the decrease in the acetic acid peak area as detected by GC.

This suggests that higher temperature of 550 °C was more favourable for the preparation of bio-oil resulting in less acidity. Furthermore, the relatively high content of acetic acid suggests that the bio-oil may need to be upgraded before it can be used as fuel in engines. BTX and related xylene derivatives compounds (Fig. 9) were found to increase with increasing temperature with the exception of 1,2,3 trimethoxy-5-methylbenzene which showed an increase at 375 °C.

4. Conclusion

Bio-oil has been successfully produced from *Parinari polyandra* Benth fruit shell using an intermediate pyrolysis process. The properties of the bio-oil obtained herein was favorably comparable with those of other bio-oils reported in the literature. The findings of the present study revealed that the pyrolysis temperature had a significant effect on the properties and quality of bio-oil obtained from Parinari seed shell. More specifically, the bio-oil produced at 550 °C had more desirable properties than those produced at 375 and 450 °C. However, the PPBFS bio-oil needs to be upgraded before it can be utilized as a fuel substitute particularly in engines as it consisted of various complex organic compounds such as acetic acid. Finally, due to the availability of PPBFS as a biomass feedstock, the parinari bio-oil is strongly suggested to be used as an alternative biofuel. Moreover, the presence of valuable compounds such as phenolic compounds in the produced bio-oil indicates potentials industrial applications as well.

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